AD-A051 054 ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND ABERD--ETC F/G 7/4
ELECTRON SPIN RESONANCE OF THE RADICAL COMPLEXES (NO2)2, (T-BUO--ETC(U)
NOV 77 C U MORGAN

UNCLASSIFIED ARBRL-MR-2799 NL

END
DATE FILMED
4-78
DDC

(12) 9

AD

BRL

MEMORANDUM REPORT ARBRL-MR-2799

ELECTRON SPIN RESONANCE OF THE RADICAL COMPLEXES $(NO_2)_2$, $(t\text{-}BuO)_2$, AND $(CH_3)_2$ IN AN ARGON MATRIX AT 10K

Cornelius U. Morgan

November 1977

USA ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
USA BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MARYLAND

Destroy this report when it is no longer needed.
Do not return it to the originator.

Secondary distribution of this report by originating or sponsoring activity is prohibited.

Additional copies of this report may be obtained from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161.

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The use of trade names or manufacturers' names in this report does not constitute indorsement of any commercial product.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER (14) MEMORANDUM REPORT ARBRL-MR-2799

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle) (6)

Electron Spin Resonance of the Radical Complexes $(NO_2)_2$, $(t\text{-}BuO)_2$, and $(CH_3)_2$ in an Argon Matrix at 10K.

5. TYPE OF REPORT & PERIOD COVERED (9)

BRL Memorandum Report.

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s) (10)

Cornelius U./Morgan

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS

U. S. Army Ballistic Research Laboratory
US Army Armament Research & Development Command
Aberdeen Proving Ground, MD 21005

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS (16)

1L161102AH43

11. CONTROLLING OFFICE NAME AND ADDRESS (11)

U. S. Army Materiel Development & Readiness Cmd
5001 Eisenhower Avenue
Alexandria, VA 22333

12. REPORT DATE (12)

November 1977

13. NUMBER OF PAGES

12 (8p.)

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)

Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

free radicals, electron spin resonance, triplett transitions, association, complex formation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

ssv/4589

In the present electron spin resonance (esr) study nitrate esters or t-butyl peroxide in an inert gas (1:100) are pyrolyzed to produce the mono-radicals NO_2, CH_3, and t-BuO. The pyrolysis products and inert gas are collected as a solid at 10K. In the solid phase some of the monoradicals associate to form the radical complexes $(NO_2)_2$, $(CH_3)_2$, and $(t\text{-}BuO)_2$. The integrated intensity of the complex in these cases is always about four orders of magnitude less than the integrated intensity of the monoradical. This fact → next Page

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

393 471

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

VV

tends to support the possibility that the complex will be formed from any monoradical that reaches a certain threshold concentration.

The electron spin resonance (esr) of a triplet state produced by the association of a H atom and methyl radical was first observed by Gordy and Morehouse[1] in solid methane at 4.2K. Trozzolo, Murray, Smolinsky, Yager, and Wasserman[2,3] have observed the esr of the ground state triplets of a number of methylenes and nitrenes. The triplet character of the esr spectra of the nitroxide biradicals, tetramethyl-2,2, 6,6, piperidinol-4 glutarate and tetramethyl-2,2,6,6, piperidinol-4 terephthalate, was demonstrated by Falle et al[4] in liquid crystal solutions.

While making an esr study of the products of the pyrolysis of gaseous nitrate esters a "$\Delta m = 2$" transition was observed at the half field position of 166.21 mT and klystron frequency ν = 9316 MHz (Figure 1A). In these experiments the nitrate ester in argon (1:100) stored in a one liter reservoir at 760 torr was passed from the reservoir through a precision leak valve for one hour at the rate of $3.6 \times 10^{-6} m^3$/ minute through a cylindrical quartz furnace heated by a coil of nichrome wire into an evacuated cryogenic refrigerator where the pyrolysis products were condensed to a solid on a sapphire rod cooled to 10K. The cryotip of the refrigerator which enclosed the cooled sapphire rod was then placed in the esr cavity and the spectra observed. In these runs whenever the "$\Delta m = 2$" transition was observed the concentration of the NO_2 radical at g = 2 was about 10^{25} spins/m^3. Because of the extremely high concentration of NO_2 in these runs it was suspected that the spectrum observed at half field was an associative complex of NO_2.

To test this theory one sample of NO_2 in argon (1:50) was passed through the furnace at a temperature of 620 K for 30 minutes and another (1:30) was run at ambient temperature for the same period and the products collected on the sapphire rod in each case. The same esr spectrum of five lines with intensity distribution of 1:2:3:2:1 and hyperfine splitting constant of 2.77 mT was observed in these two cases as with the nitrate esters (Figure 1A). From the results of these runs it was concluded that the spectrum was produced by the interaction of two equivalent nitrogen atoms contained in a radical complex such as $(NO_2)_2$ with the free electrons. This spectrum did not decrease in intensity after several hours of monitoring at 10 K. In these two NO_2 runs, the concentration of NO_2 observed was 10^{26} spins/m^3. The integrated intensity of the spectrum of the NO_2 radical in these two cases was about four orders of magnitude higher than the integrated intensity of the $(NO_2)_2$ spectrum.

---

[1] *W. Gordy and R. Morehouse, Phys. Rev. 151, 207 (1966).*

[2] *A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, J. Am. Chem. Soc., 85, 2526 (1963).*

[3] *E. Wasserman, G. Smolinsky, and W. A. Yager, J. Am. Chem. Soc., 86, 3166 (1964).*

[4] *H. R. Falle, G. R. Luckhurst, H. Lemaire, Y. Marechal, A. Rassat, and P. Rey, Mol. Phys. 11, 49 (1966).*

In some similar thermal decomposition work on t-butyl peroxide in argon, two different "$\Delta m = 2$" transition spectra were observed. When t-butyl peroxide in argon (1:100) was pyrolyzed at 730 K, a single line spectrum due to a "$\Delta m = 2$" transition was observed (Figure 1B). This spectrum observed at a field of 164.43 mT was produced by the complex $(t\text{-BuO})_2$. The concentration of t-BuO radical at g = 2 was 10^{25} spins/m^3. The integrated intensity of the t-BuO radical spectrum in this run was four orders of magnitude higher than the integrated intensity of the spectrum of the $(t\text{-BuO})_2$ complex.

When a mixture of t-butyl peroxide in argon (1:100) was heated at 600 K, two "$\Delta m = 2$" spectral transitions were observed (Figure 1C). The most intense of these appeared at a field of 166.17 mT. The spectrum consisted of seven lines with an intensity distribution of 1:6:15:20:15:6:1 and hyperfine splitting constant of 1.14 mT. This spectrum was produced by the $(CH_3)_2$ complex by the interaction of six equivalent protons with the free electrons. This spectrum is displaced about the base line due to the presence of the single line spectrum of $(t\text{-BuO})_2$. The concentration of methyl radicals at g = 2 in this run is 10^{25} spins/m^3. The concentration of the t-BuO radical in this instance is masked by the high concentration of the methyl radical. Complexes $(CH_3)_2$ and $(t\text{-BuO})_2$ are stable at 10 K and no change in concentration is noticed after an hour of monitoring. The integrated intensity of the methyl radical spectrum in this run was four orders of magnitude higher than the integrated intensity of the spectrum of the $(CH_3)_2$ complex.

Since these radical complexes have been observed in each of the few cases that have been examined, the possibility exists that when the concentration of any radical reaches a certain threshold value, the "$\Delta m = 2$" transition complex should be observed.

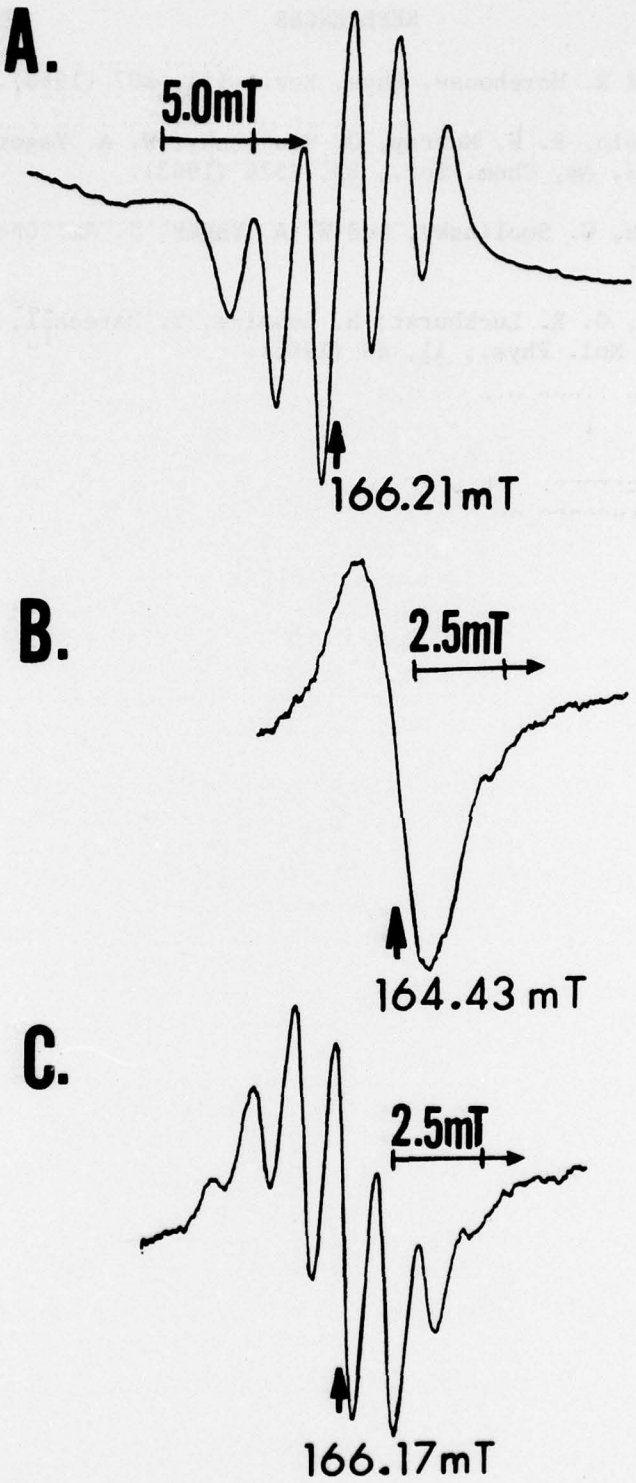

Figure 1. Spectra of Radical Complexes: A. $(NO_2)_2$; B. $(t\text{-}BuO)_2$; and C. $(CH_3)_2$ and $(t\text{-}BuO)_2$

REFERENCES

1. W. Gordy and R. Morehouse, Phys. Rev., 151, 207 (1966).

2. A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, J. Am. Chem. Soc., 85, 2526 (1963).

3. E. Wasserman, G. Smolinsky, and W. A. Yager, J. Am. Chem. Soc., 86, 3166 (1964).

4. H. R. Falle, G. R. Luckhurst, H. Lemaire, Y. Marechal, A. Rassat, and P. Rey, Mol. Phys., 11, 49 (1966).

DISTRIBUTION LIST

No. of Copies	Organization
12	Commander Defense Documentation Center ATTN: DCC-TCA Cameron Station Alexandria, VA 22314
1	Director Defense Advanced Research Projects Agency ATTN: C. R. Lehner 1400 Wilson Boulevard Arlington, VA 22209
2	Director Institute for Defense Analyses ATTN: Dr. H. Wolfhard R. T. Oliver 400 Army-Navy Drive Arlington, VA 22202
1	Commander US Army Materiel Development and Readiness Command ATTN: DRCDMA-ST 5001 Eisenhower Avenue Alexandria, VA 22333
1	Commander US Army Aviation Research and Development Command ATTN: DRSAV-E 12th and Spruce Streets St. Louis, MO 63166
1	Director US Army Air Mobility Research and Development Laboratory Ames Research Center Moffett Field, CA 94035
1	Commander US Army Electronics Command ATTN: DRSEL-RD Ft. Monmouth, NJ 07703
1	Commander US Army Missile Research and Development Command ATTN: DRDMI-R Redstone Arsenal, AL 35809
1	Commander US Army Tank Automotive Development Command ATTN: DRDTA-RWL Warren, MI 48090
2	Commander US Army Mobility Equipment Research & Development Command ATTN: Tech Doc Ctr, Bldg 315 DRSME-RZT Ft. Belvoir, VA 22060
1	Commander US Army Armament Materiel Readiness Command ATTN: DRSAR-LEP-L, Tech Lib Rock Island, IL 61202
3	Commander US Army Armament Research and Development Command ATTN: C. Lenchitz J. Lannon D. Downs Dover, NJ 07801
1	Commander US Army White Sands Missile Range ATTN: STEWS-VT WSMR, NM 88002
1	Commander US Army Watervliet Arsenal ATTN: R. Thierry/Code SARWV-RD Watervliet, NY 12189

DISTRIBUTION LIST

No. of Copies	Organization
1	Commander US Army Materials and Mechanics Research Center ATTN: DRXMR-ATL Watertown, MA 02172
1	Commander US Army Natick Research and Development Command ATTN: DRXRE, Dr. D. Sieling Natick, MA 01762
1	Director US Army TRADOC Systems Analysis Activity ATTN: ATAA-SL, Tech Lib WSMR, NM 88002
1	Commander US Army Research Office ATTN: Tech Lib P.O. Box 12211 Rsch Triangle Park, NC 27706
1	Chief of Naval Research ATTN: Code 473 800 N. Quincy Street Arlington, VA 22217
1	Commander US Naval Sea Systems Cmd ATTN: J. W. Murrin (NAVSEA-0331) National Center Bldg 2, Rm 6E08 Washington, DC 20360
2	Commander US Naval Surface Weapons Ctr White Oak Laboratory ATTN: S. J. Jacobs R. R. Bernecker, R13 Silver Spring, MD 20910
1	Commander US Naval Surface Weapons Center ATTN: Library Br, DX-21 Dahlgren, VA 22448
1	Commander US Naval Underwater Systems Center Energy Conversion Department ATTN: R. S. Lazar/Code 5B331 Newport, RI 02840
2	Commander US Naval Weapons Center ATTN: Dr. R. Derr Mr. H. Bradley China Lake, CA 93555
1	Commander US Naval Research Laboratory ATTN: Code 6180 Washington, DC 20375
3	Superintendent US Naval Postgraduate School ATTN: Tech Lib Dr. David Netzer Dr. Allen Fuhs Monterey, CA 93940
3	Commander US Naval Ordnance Station ATTN: S. E. Mitchell C. B. Dale Tech Lib Indian Head, MD 20640
2	AFOSR ATTN: J. F. Masi Dr. B. T. Wolfson Bolling AFB, DC 20332

DISTRIBUTION LIST

No. of Copies	Organization
2	AFRPL (DYSC) ATTN: Dr. D. George Mr. J. N. Levine Edwards AFB, CA 93523
1	Lockheed Palo Alto Rsch Labs ATTN: Tech Info Ctr 3251 Hanover Street Palo Alto, CA 94304
1	Aerojet Solid Propulsion Co. ATTN: Dr. P. Micheli Sacramento, CA 95813
1	ARO Incorporated ATTN: Mr. N. Dougherty Arnold AFS, TN 37389
1	Atlantic Research Corporation ATTN: Dr. M. K. King 5390 Cherokee Avenue Alexandria, VA 22314
1	AVCO Corporation AVCO Everett Research Lab Div ATTN: D. Stickler 2385 Revere Beach Parkway Everett, MA 02149
2	Calspan Corporation ATTN: Dr. E. B. Fisher A. P. Trippe P.O. Box 235 Buffalo, NY 14221
1	ENKI Corporation ATTN: M. I. Madison 9015 Fulbright Avenue Chatsworth, CA 91311
1	Foster Miller Associates, Inc. ATTN: A. J. Erickson 135 Second Avenue Waltham, MA 02154
1	General Electric Company Armament Department ATTN: M. J. Bulman Lakeside Avenue Burlington, VT 05402
1	General Electric Company Flight Propulsion Division ATTN: Tech Lib Cincinnati, OH 45215
1	Paul Gough Associates, Inc. ATTN: Dr. P. S. Gough P.O. Box 1614 Portsmouth, NH 03801
2	Hercules Incorporated Alleghany Ballistic Lab ATTN: Dr. R. Miller Tech Lib Cumberland, MD 21501
2	Hercules Incorporated Bacchus Works ATTN: Dr. D. Pilcher Dr. R. Simmons Magna, UT 84044
1	IITRI ATTN: Dr. M. J. Klein 10 West 35th Street Chicago, IL 60615
1	Olin Corporation Badger Army Ammunition Plant ATTN: J. Ramnarace Baraboo, WI 53913
2	Olin Corporation New Haven Plant ATTN: R. L. Cook D. W. Riefler 275 Winchester Avenue New Haven, CT 06504

DISTRIBUTION LIST

No. of Copies	Organization
1	Physics International Company 2700 Merced Street San Leandro, CA 94577
1	Pulsepower Systems, Inc. ATTN: L. C. Elmore 815 American Street San Carlos, CA 94070
1	Science Applications, Inc. ATTN: Dr. R. B. Edelman 23146 Cumorah Crest Woodland Hills, CA 91364
2	Rockwell International Corp. Rocketdyne Division ATTN: Dr. C. Obert Dr. J. E. Flanagan 6633 Canoga Avenue Canoga Park, CA 91304
2	Rockwell International Corp. Rocketdyne Division ATTN: Mr. W. Haymes Tech Lib McGregor, TX 76657
1	Shock Hydrodynamics, Inc. ATTN: Dr. W. H. Anderson 4710-16 Vineland Avenue North Hollywood, CA 91602
1	Thiokol Corporation Elkton Division ATTN: E. Sutton Elkton, MD 21921
3	Thiokol Corporation Huntsville Division ATTN: Dr. D. Flanigan Dr. R. Glick Tech Lib Huntsville, AL 35807
2	Thiokol Corporation Wasatch Division ATTN: Dr. John Peterson Tech Lib P.O. Box 524 Brigham City, UT 84302
1	TRW Systems Group ATTN: Dr. H. Korman One Space Park Redondo Beach, CA 90278
2	United Technology Center ATTN: Dr. R. Brown Tech Lib P.O. Box 358 Sunnyvale, CA 94088
1	Universal Propulsion Co. ATTN: H. J. McSpadden P.O. Box 546 Riverside, CA 92502
1	*Battelle Memorial Institute* ATTN: Tech Lib 505 King Avenue Columbus, OH 43201
1	Brigham Young University Dept of Chemical Engineering ATTN: Dr. M. Beckstead Provo, UT 84601
1	California Institute of Technology ATTN: Prof. F. E. C. Culick 204 Karman Lab, Mail Stop 301-46 1201 E. California Street Pasadena, CA 91125
1	Case Western Reserve Univ. Division of Aerospace Sciences ATTN: Prof. J. Tien Cleveland, OH 44135

DISTRIBUTION LIST

No. of Copies	Organization
1	Duke University Department of Physics ATTN: Dr. Walter Gordy Durham, NC
3	Georgia Institute of Technology School of Aerospace Engineering ATTN: Prof. B. T. Zinn Prof. E. Price Prof. W. C. Strahle Atlanta, GA 30332
1	Johns Hopkins University Applied Physics Laboratory Chemical Propulsion Information Agency ATTN: Mr. T. Christian Johns Hopkins Road Laurel, MD 20810
1	Massachusetts Institute of Technology Dept of Mechanical Engineering ATTN: Prof. T. Toong Cambridge, MA 02139
1	Pennsylvania State University Dept of Mechanical Engineering ATTN: Prof. K. Kuo University Park, PA 16801
3	Princeton University Forrestal Campus Library ATTN: Prof. M. Summerfield Dr. L. Caveny Tech Lib P.O. Box 710 Princeton, NJ 08540
2	Purdue University School of Mechanical Engineering ATTN: Prof. J. Osborn Prof. J. D. Hoffman TSPC Chaffee Hall West Lafayette, IN 47906
1	Rutgers State University Dept of Mechanical and Aerospace Engineering ATTN: Prof. S. Temkin University Heights Campus New Brunswick, NJ 08903
1	Southwest Research Institute Fire Research Section ATTN: W. H. McLain P.O. Drawer 28510 San Antonio, TX 78228
1	Stanford Research Institute Propulsion Sciences Division ATTN: Tech Lib 333 Ravenswood Avenue Menlo Park, CA 94024
1	Stevens Institute of Technology Davidson Laboratory ATTN: Prof. R. McAlevy III Hoboken, NJ 07030
1	University of California San Diego AMES Department ATTN: Prof. F. Williams P.O. Box 109 La Jolla, CA 92037
1	University of Illinois Dept. of Aeronautical Engineering ATTN: Prof. H. Krier Transportation Bldg, Rm 105 Urbana, IL 61801
1	University of Minnesota Dept. of Mechanical Engineering ATTN: Prof. E. Fletcher Minneapolis, MN 55455

DISTRIBUTION LIST

No. of Copies	Organization
2	University of Utah Dept. of Chemical Engineering ATTN: Prof. A. Baer Prof. G. Flandro Salt Lake City, UT 84112

Aberdeen Proving Ground

Marine Corps LnO
Dir, AMSAA